2. Evaluation of the Base Mechanism

The spreadsheet workbook containing the base mechanism as received from Dr. Carter on April 19, 1999 and updated on May 5 was evaluated. It consisted of 4 separate spreadsheets, "Species Listing", "Reaction Listing", "Base Mech Notes" and "Refs".

Suggestions Made Regarding the "Species Listings".

Constant Species

The units for the defaults of the Constant Species should be defined. The units of O2, M and H2O appear to be ppm while the unit for light appears to be a multiplier of unity.

HV, light, is listed under Constant Species and characterized as a Type "Con". Although HV is not a chemical species it is not a constant in the atmosphere. It is suggested that HV be moved to its own category for clarity.

The assignments for the number of carbon atoms (nC), the number of reactive nitrogen atoms (nN) and the radical character (nR) for the constant species are correct for the constant species.

Active Inorganic Species

The active inorganic species list is relatively complete. It could be argued that CO should be listed here but since CO is a very important product of organic reactions it is also understandable that it is placed under Explicit Reactive Organic Product Species.

H_2 should be considered as either a constant species that reacts or as an active inorganic species because the reaction H_2 + HO is a sink for HO that occurs with a rate that is 30% that of the reaction CH_4 + HO for typical atmospheric conditions (Stockwell et al., 1997).

Dr. Carter may want to consider adding SO_2 as an active species. Although SO_2 is not greatly important for incremental reactivity applications the mechanism may be used for other applications, such as aerosol formation studies, where this chemistry can be important. The sulfate produced should be added as a Non-Reacting Species, see below.

It is not clear how "Act* differs from "Act".

Although the name nitrogen pentoxide is commonly used it would be more correct to call it dinitrogen pentoxide.

The assignments for the number of carbon atoms (nC), the number of reactive nitrogen atoms (nN) and the radical character (nR) for the constant species are correct for the active inorganic species.

Active Radical Species and Operators

As mentioned above it is not clear how "Act* differs from "Act".

The number of active radicals listed appear to be adequate for the base mechanism.

For complete clarity the R2O2. radical could be described as "Peroxy Radical Operator representing NO to NO2 conversion without HO2 formation".

It seems surprising that the radical character (nR) of R2O2 is zero since it is a radical operator.

Other Steady State Radical Species

The category title should be changed because there are no other steady state radical species. It is suggested that the title be changed to Radical Species Treated as in Steady State.

The species treated as steady state are reasonable due to their short lifetime in the atmosphere.

The assignments for nC, nN and nR for the constant species are correct for the radical species treated as in steady state. The oxygen atoms might be labeled as bi-radicals.

PAN and PAN Analogues

The number and nature of the species included in this category are adequate for the base mechanism. The species are clearly named.

The nC given for PBZN is consistent with the BZCO-O2 radical.

The other nC, nN and nR for PAN and PAN Analoges are correct.

Explicit Reactive Organic Product Species

CO could be listed as an active inorganic species because most of CO comes from direct emissions and not the chemical reactions of organic species. However, it is an important product so its inclusion in this category is understandable.

The number and nature of the species included in this category are adequate for the base mechanism. The species are clearly named.

The nC, nN and nR for the explicit reactive organic product species are correct.

Lumped Reactive Organic Product Species

The number, nature and descriptions of the species included in this category are adequate for the base mechanism.

Is there data that suggests that the average carbon number of higher organic peroxides, ROOH, is really as high as 3? I would guess that it is closer to 2.

Non-Reacting Species

Although H2 should be treated as a constant it is not unreactive. It is a sink for HO radicals that should not be ignored.

If SO2 were to be included in the mechanism than sulfate should be included here.

Low Reactivity Compounds or Unknown Products Represented as Unreactive

Treatment of organic acids and methyl nitrate as unreactive is appropriate.

I would expect the stabilizated products from the Crigiee biradicals to be too reactive to be treated in this category. Would it be better to treat them as something at least like ketones?

Primary Organics Represented Explicitly

I can easily accept that CH4 belongs in this category but given the relative complexity of isoprene chemistry it is not accurate to place it in this category.

Following used in reports

These are definitions that are reasonable and most have been used by Dr. Carter previously.

Biogenic Compounds in the EKMA Simulations

These are definitions that are reasonable.

Lumped species used to represent the Base ROG mixture in the EKMA model simulations.

These are definitions that are reasonable and within standard practice.

General comments on the Base Mechanism

Representation of Radical Species

Rapidly Reacting Radicals

The treatment of the decomposition of excited Crigiee biradicals is within the present state of knowledge. It is also reasonable to assume that the Crigiee biradicals react with water to produce organic acids. The reaction of Crigiee biradicals with SO_2 could be important only in rare plumes that are relatively dry with high concentrations of SO_2 and alkenes.

Explicitly Represented Organic Radicals

The revision of the mechanism to include representation of a few organic radical species as explicit represents a significant a improvement in the mechanism. Dr. Carter provides good justification for this treatment of methyl peroxy radicals, acyl peroxy radicals t-butoxy radicals, phenoxy radicals, nitro-phenoxy radicals and the formaldehyde + HO_2 intermediate.

There is much uncertainty in the fate of phenoxy radicals and nitro-phenoxy radicals. More research will be required to determine the fate of these radicals produced from aromatic oxidation.

Reactions of Common Products

Explicitly Represented and Lumped Molecule Products

Glyoxal (GLY).
The quantum yields of glyoxal were increased by a factor near 1.4 on the basis of fits to chamber data. These quantum yields are uncertain and Dr. Carter is correct to note that new direct measurements of glyoxal quantum yields as a function of wavelength are required to reduce this uncertainty.

Methyl Glyoxal (MGLY) and Other Higher α-dicarbonyl aldehydes.

Dr. Carter is correct in accepting the revised absorption cross sections of Moortgat for methyl glyoxal.

Phenol (PHEN) and Cresols (CRES).

More data is required for these compounds but given the available data Dr. Carter's treatment of these reactions is reasonable.

Lumped Parameter Products

Derivation of PROD2 and RNO3 Mechanisms.
From the discussion it is not clear why PROD2 which is derived from a set of model species with 7 carbon atoms is represented as having only 6 carbon atoms in the mechanism. This may be correct but the reason for this approach is not clear.

Uncharacterized Aromatic Ring Fragmentation Products

The use of DCB species to represent uncharacterized aromatic ring fragmentation products is a significant advance over the former AFGn treatment. More data will be required to better characterize this aspect of aromatic chemistry.

Unreactive Product Species

The discussion of unreactive product species is reasonable. Although the production of H_2 due to tropospheric reactions is insignificant, the effect of the background concentration of H_2 on HO levels is not. The rate of the HO reaction with H_2 is about 30% of its rate with CH_4. The discussion of H_2 should be revised accordingly.